

Superfund Records Center
SITE: Ciba-Geigy
BL. SAK: 19.00
OTTERB: 651247

8/7/11

Frank -

Enclosed are the data validation
memos for Ciba Geigy dioxin
samples. A copy of those memos along
with the raw data was sent
to Alliance. If you have
any questions please call me.

Scott Clifford
ESAT DPO
860-4631



SEMS DocID 651247



ESAT PROJECT
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PHONE: 617-229-2050

July 26, 1991
0-1-07-03

Rec'd 0
8-8-91 F.B.

Mr. Dennis Gagne
Regional Sample Control Custodian
U.S. Environmental Protection Agency
90 Canal Street
Boston, Massachusetts 02114

Re: TID No. 01-9105-40
SAS No. 6208A, SDG No. 6208A-01
Triangle Laboratory
Ciba Geigy
Cranston, RI
Dioxin: 6/Aqueous/6208A-01, 6208A-02, 6208A-03,
6208A-04, 6208A-05, 6208A-06

Dear Mr. Gagne:

A validation was performed on the dioxin/furan analytical data for 6 aqueous samples collected by Alliance Technologies at the Ciba Geigy site. The samples were analyzed according to SAS 6208A specifications. The data were evaluated based on the following parameters:

- data completeness
 - PEM samples
 - * ● window defining mix
 - * ● calibrations
 - * ● column performance
 - * ● internal standards
 - recovery standards
 - method blanks
 - * ● matrix spike/matrix spike duplicates
 - * ● field duplicates
 - * ● concentration/EMPC/EDL
 - total congener concentrations
 - toxic equivalency factor
- * - All criteria were met for this parameter.

Table I summarizes the validation recommendations which were based on the following information:



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Data Completeness

The laboratory was contacted on July 11, 1991 to request submission of additional raw data for all standards, including area counts. All requested information was received from the laboratory on July 24, 1991.

PEM Samples

No PEM samples were submitted with this SDG since all the samples were aqueous. PEM samples were submitted to this laboratory with SAS 6149A, SDG 6149A-01. These PEM samples were analyzed on April 2, 1991 and the results were acceptable. No action is necessary.

Calibration

The 3/8/91 initial calibration did not meet the %RSD criteria of 15.0% for 12378-PeCDD(16.7%). No action is necessary for either 12378-PeCDD or total PeCDDs since no positive results were detected.

Recovery Standards

Recovery Standard Response

Samples 6208A-02, 6208A-03 and 6208A-04 had area counts for recovery standards outside the -50% to +100% limits. Recovery standard ^{13}C -1234-TCDD in samples 6208A-02 and 6208A-03 was more than 100% higher than the daily CC3 standard. EMPC results for Total TCDD will be estimated (J) and non-detected results for 2378-TCDD will be accepted in samples 6208A-02 and 6208A-03. Recovery standard ^{13}C -123789-HxCDD in sample 6208A-04 was less than -50% lower than the daily CC3 standard. Since low recovery may indicate a sensitivity problem as well as a inconsistency problem, non-detected Total HxCDD and substituted 2378-HxCDD isomers will be estimated (UJ) in sample 6208A-04.

Method Blanks

A potential but unconfirmed TCDD peak (no apparent M-[COCl] $^+$, ion ratio outside QC criteria) was present within



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the retention time window at greater than the 5% blank contaminant threshold. Potential TCDD was determined at more than 38% of the TCDD internal standard resulting in an EMPC for DFBLK1 of 16.391 ng/L. Because of the possible blank contamination of TCDD all Total TCDD EMPC results will be estimated (J). An EMPC for Total TCDF was also reported in the blank but no qualification of the samples is necessary since the value was less than 5% of the internal standard threshold for unconfirmed dioxin/furans.

Field Duplicates

Reported results for Total TCDF in field duplicate samples 6208A-01 and 6208A-02 were above the standard precision criteria of 30% for aqueous samples with an %RPD of 32%. Estimate (J) the Total TCDF results for samples 6208A-01 and 6208A-02 because of poor reproducability.

Total Congener Concentrations

The laboratory did not report or calculate an EDL/EMPC for Total PeCDD for sample 6208A-03. Since no possible positive results were noted by the reviewer within the retention time window, the EDL from the 12378-PeCDD (0.293) is reported as the EDL for the Total PeCDD.

Toxicity Equivalence Factor

The laboratory used an incorrect toxicity equivalence factor in the calculation of the Total TEF. The laboratory used a factor of 0.05 for 23478-PeCDF rather than 0.5 according to the "Interim Procedure for Estimating Risk Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-dioxins and Dibenzofurans (CDDs and CDFs)", EPA625-3-89-016, March 1989. No TEF-adjusted concentrations were affected since no positive results or EMPCs were calculated for this compound.

Data Summary

The results for the dioxin/furan analyses were acceptable overall. Method blank contamination caused qualification of Total TCDD results for all samples.

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Qualification of Total TCDD in samples 6208A-02 and 6208A-03 and of substituted HxCDD and Total HxCDD results in sample 6208A-04 was necessary due to recovery standards outside the acceptable range relative to the continuing calibration standard. Qualification of Total TCDF was necessary in samples 6208A-01 and 6208A-02 due to poor reproducibility of the field duplicates.

Very truly yours,

ROY F. WESTON, INC.

Dean Gouveia

Dean A. Gouveia
Organic Data Reviewer

Chery Blaine

Chery Blaine
Senior Organic
Data Reviewer

John J. Hagopian

John J. Hagopian, P. G.
Team Manager
ESAT Region I

/dag
Enclosure(s)
cc: D. Szaro

TABLE I
Ciba Geigy
SAS 6208A

PCDD/PCDF ANALYSES

SAMPLE NUMBER: 6208A-01 6208A-02 6208A-03 6208A-04 6208A-05 6208A-06

DIOXINS

2,3,7,8-TCDD	A	A	A	A	A	A
1,2,3,7,8-PeCDD	A	A	A	A	A	A
1,2,3,4,7,8-HxCDD	A	A	A	J ¹	A	A
1,2,3,6,7,8-HxCDD	A	A	A	J ¹	A	A
1,2,3,7,8,9-HxCDD	A	A	A	J ¹	A	A
1,2,3,4,6,7,8-HpCDD	A	A	A	A	A	A
OCDD	A	A	A	A	A	A

FURANS

2,3,7,8-TCDF	A	A	A	A	A	A
1,2,3,7,8-PeCDF	A	A	A	A	A	A
2,3,4,7,8-PeCDF	A	A	A	A	A	A
1,2,3,4,7,8-HxCDF	A	A	A	A	A	A
1,2,3,6,7,8-HxCDF	A	A	A	A	A	A
2,3,4,6,7,8-HxCDF	A	A	A	A	A	A
1,2,3,7,8,9-HxCDF	A	A	A	A	A	A
1,2,3,4,6,7,8-HpCDF	A	A	A	A	A	A
1,2,3,4,7,8,9-HpCDF	A	A	A	A	A	A
OCDF	A	A	A	A	A	A

A - Accept the data.

J¹ - Estimate (UJ) the non-detected values since the recovery standards were below the acceptable range as determined by the continuing calibration standard. Low recoveries indicate reduced sensitivity for the associated compounds which may cause possible false reporting of negative results.

Data Summary Key

- A - Acceptable data.
- J - The associated numerical value is an estimated quantity.
- R - Reject data due to quality control criteria. The data are unusable (compound may or may not be present). Resampling and reanalysis is necessary for verification.
- U - The compound was analyzed for but was not detected. The associated numerical value is the sample quantitation limit.
- UJ - The compound was analyzed for, but was not detected. The sample quantitation limit is an estimated quantity.
- - The compound was analyzed for, but was not detected. The sample quantitation limit is the same as the CRQL presented.

SITE: CIBA GEIGY - CRANSTON, RI

CASE/SAS NO: 6208A

Sample No	6208A-01		6208A-02		6208-03	
Matrix	AQUEOUS		AQUEOUS		AQUEOUS	
TCDD/TCDF Conc	ng/L	DL/EMPC*	ng/L	DL/EMPC*	ng/L	DL/EMPC*
2,3,7,8-TCDD	U	0.040	U	0.045	U	0.098
1,2,3,7,8-PeCDD	U	0.117	U	0.113	U	0.293
1,2,3,4,7,8-HxCDD	U	0.298	U	0.224	U	0.430
1,2,3,6,7,8-HxCDD	U	0.265	U	0.186	U	0.358
1,2,3,7,8,9-HxCDD	U	0.273	U	0.218	U	0.419
1,2,3,4,6,7,8-HpCDD	0.252		U	0.224	U	0.455
OCDD	1.82		0.404		1.53	
2,3,7,8-TCDF	0.098		0.126		U	0.074
1,2,3,7,8-PeCDF	U	0.103	U	0.051	U	0.181
2,3,4,7,8-PeCDF	U	0.102	U	0.053	U	0.189
1,2,3,4,7,8-HxCDF	U	0.117	U	0.079	U	0.197
1,2,3,6,7,8-HxCDF	U	0.104	U	0.070	U	0.176
2,3,4,6,7,8-HxCDF	U	0.097	U	0.067	U	0.167
1,2,3,7,8,9-HxCDF	U	0.141	U	0.115	U	0.288
1,2,3,4,6,7,8-HpCDF	U	0.134	U	0.111	U	0.240
1,2,3,4,7,8,9-HpCDF	U	0.170	U	0.179	U	0.388
OCDF		0.116*	U	0.011	U	0.016
TOTAL TCDD		17.4* J		20.9* J		15.3* J
TOTAL PeCDD	U	0.117	U	0.113	U	0.293
TOTAL HxCDD	U	0.298	U	0.224	U	0.430
TOTAL HpCDD	0.25		U	0.224	U	0.455
TOTAL TCDF	11.4 J	12.6*	15.7 J	16.6*		0.708*
TOTAL PeCDF	U	0.103	U	0.053	U	0.189
TOTAL HxCDF	U	0.141	U	0.115	U	0.288
TOTAL HpCDF	U	0.170	U	0.179	U	0.388
TOXICITY EQUIVALENCY	0.0143		0.0130		0.0153	
DILUTION FACTOR	1		1		1	
DATE OF RECEIPT	04/20/91		04/20/91		04/20/91	
SAMPLE EXTRACTION DATE	04/25/91		04/25/91		04/25/91	
ANALYSIS DATE	05/07/91		05/01/91		05/01/91	
GC/MS I.D.	70E		70E		70E	

SITE: CIBA GEIGY - CRANSTON, RI

CASE/SAS NO: 6208A

Sample No	6208A-04		6208-05		6208A-06	
Matrix	AQUEOUS			AQUEOUS		
TCDD/TCDF Conc	ng/L	DL/EMPC*	ng/L	DL/EMPC*	ng/L	DL/EMPC*
2,3,7,8-TCDD	U	0.115	U	0.068	U	0.100
1,2,3,7,8-PeCDD	U	0.514	U	0.158	U	0.416
1,2,3,4,7,8-HxCDD	UJ	0.556	U	0.182	U	0.287
1,2,3,6,7,8-HxCDD	UJ	0.463	U	0.151	U	0.255
1,2,3,7,8,9-HxCDD	UJ	0.542	U	0.177	U	0.263
1,2,3,4,6,7,8-HpCDD	U	0.596	U	0.146	U	0.166
OCDD	2.33		0.650		0.751	
2,3,7,8-TCDF	U	0.079	U	0.049	U	0.070
1,2,3,7,8-PeCDF	U	0.323	U	0.140	U	0.319
2,3,4,7,8-PeCDF	U	0.335	U	0.146	U	0.315
1,2,3,4,7,8-HxCDF	U	0.246	U	0.074	U	0.106
1,2,3,6,7,8-HxCDF	U	0.220	U	0.066	U	0.094
2,3,4,6,7,8-HxCDF	U	0.208	U	0.063	U	0.088
1,2,3,7,8,9-HxCDF	U	0.359	U	0.108	U	0.128
1,2,3,4,6,7,8-HpCDF	U	0.256	0.085		U	0.096
1,2,3,4,7,8,9-HpCDF	U	0.414	U	0.132	U	0.122
OCDF	U	0.481	26.6		U	0.177
TOTAL TCDD		18.8* J		17.5* J		19.0* J
TOTAL PeCDD	U	0.514	U	0.158	U	0.416
TOTAL HxCDD	UJ	0.556	U	0.182	U	0.287
TOTAL HpCDD	U	0.596	U	0.146	U	0.166
TOTAL TCDF	0.88	1.36*		0.369*		0.691*
TOTAL PeCDF	U	0.335	U	0.146	U	0.319
TOTAL HxCDF	U	0.359	U	0.108	U	0.128
TOTAL HpCDF	U	0.414	0.08		U	0.122
TOXICITY EQUIVALENCY	0.00232		0.0281		0.000751	
DILUTION FACTOR	1		1		1	
DATE OF RECEIPT	04/20/91		04/20/91		04/20/91	
SAMPLE EXTRACTION DATE	04/25/91		04/25/91		04/25/91	
ANALYSIS DATE	05/02/91		05/01/91		05/07/91	
GC/MS I.D.	70E		70E		70E	

ATTACHMENT I

DIOXIN DATA REVIEW WORKSHEET

Regional Review of Dioxin Data Package

The hard copied (laboratory name TRIANGLE LABS) data package received at Region I has been reviewed and the quality assurance and performance data summarized. The data review included:

Case No.

Sampling Date 4/18/91

SAS No. 6208A

Matrix water (aqueous)

No. of Samples 6

Date Received by Laboratory 4/20/91

Shipping Date 4/19/91

Sample Nos.: 6208A - 01, 02, 03, 04, 05, 06

PEM Nos.

Fortified Std

Laboratory ID

EPA Identification No.

Fortified Blank

None

None

The general criteria used to determine the performance were based on an examination of:

- | | |
|--|--|
| <input type="radio"/> PEM Samples | <input type="radio"/> Internal Standard response |
| <input type="radio"/> Initial and continuing calibrations | <input type="radio"/> Recovery standard areas |
| <input type="radio"/> Retention time marker solutions | <input type="radio"/> Matrix spike analysis |
| <input type="radio"/> Estimated maximum possible concentration | <input type="radio"/> Duplicate analysis |
| | <input type="radio"/> Method blanks |
| | <input type="radio"/> Instrument sensitivity check |
| | <input type="radio"/> Chromatographic resolution |

Definition of Qualifiers

- A - Acceptable data
J - Approximate data due to quality control criteria
R - Reject data due to quality control criteria
U - Not detected
S - $[M-COCl]^+$ ion did not meet S/N ratio >2.5 requirement
H - Did not meet the ion abundance criteria

DIOXIN DATA REVIEW WORKSHEET

I PEM SAMPLES

A.	<u>Fortified Blank</u>	<u>Laboratory ID</u>	<u>EPA ID</u>	<u>Laboratory No.</u>
	<u>Compounds Found</u>	<u>Concentration</u>	<u>Expected Concentration</u>	
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
B.	<u>Fortified Std.</u>	<u>Laboratory ID</u>	<u>EPA ID</u>	<u>Laboratory No.</u>
	<u>Compounds Found</u>	<u>Concentration</u>	<u>EPA 95% Prediction Level</u>	
	<u>2,3,7,8-TCDD</u>	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____
	_____	_____	_____	_____

Action: If the 2,3,7,8-TCDD reported in the fortified standard is beyond the 95 % prediction level or a false positive for 2,3,7,8-TCDD in the blank is reported, reject all data.

No PE samples were issued with this SAS.

All samples are aqueous

PE samples for recent ~~the~~ case was analyzed by one lab on 4/2/91 & results were acceptable.

III. INITIAL AND CONTINUING CALIBRATION

Date of Initial Calibration: 3/8/91

Date of Continuing Calibration: 5/1/91, 5/7/91

Action: % RSD >15% approximate all the associated data (J or UJ)
% D >30% approximate all the associated data.

Was a CC3 analyzed just prior to sample analysis and every 12 hours? OK

5/1/91 ~~Window defining~~ Mix 15:35

CC3	16:35
Method blank	17:28
Samples: 6208A-05	18:23
Three - 6208A-04	1:18

5/7/91 Window defining mix 9:02.

CC3 9:57

samples 6208A-05/00 KIVD

6208A-06 RI - 14;21

④ Since full 5-point calibrations are not required for these compounds no action is necessary.

Note that the laboratory used the average RF of the calibrated isomers rather than the lowest RF of the ²³⁷^{Tl} isomer for calculation of total amounts. Using the lowest RF would overestimate the amounts.

Initial Calibration

3/8/91

Ratios all w/in limits ✓

$$\text{CC1 } 2,3,7,8\text{-TCDD} \quad \frac{2958}{392} = 0.760 \quad \checkmark \quad \text{Form VI PCDD-2 reported} = 0.765 - 0.770$$

$$\text{CC2 HPDF} \quad \frac{924}{882} = 1.048 \quad \checkmark \quad \text{Form VI PCDD-2 reported} = 1.048$$

$$\text{CC4 OCDF} \quad \frac{6972}{8029} = 0.868 \quad \checkmark \quad \text{Form VI PCDD-2 reported} = 0.870$$

~~RRF~~

$$\text{CC3 } 2,3,7,8\text{-PeCDF} = \frac{(4488.06 + 2865.43) \times .50}{(5099.43 + 6464.26) \times .50} = 0.6359 \quad \checkmark \quad \text{Form VI PCDD-1(pg 38) 0.637}$$

$$\text{PeCDF} = \frac{(2747 + 1746) \times .5}{(640 + 2083) \times .5}$$

~~RRF~~

$$\text{CC1 } 1,2,3,4,6,7,8\text{-HxCDD} \quad \frac{(676.85 + 625.11) \times .50}{(2439.01 + 1910.76) \times .25} = 0.5986 \quad \checkmark \quad \text{reported 0.599}$$

~~RRF~~

$$\text{CC5 } 2,3,7,8\text{-TCDF} \quad \frac{(35983.48 + 457467.24) \times .50}{(7404.61 + 9267.41) \times .200} = 1.218 \quad \checkmark \quad \text{reported 1.218}$$

% RSDs

1,2,3,7,8 - PeCDD ~~17.7%~~ 16.7% outside 15.0% limits

2,3,4,6,7,8 - HxCDF 15.1% outside 15.0% limits not required

1,2,3,4,7,8,9 - HpCDF 15.2% outside 15.0% limits by SOW

RT ✓ w/in windows

S/N ✓ ok all ~~were~~ S/N > 2.5 for unlabelled & > 10 for labelled

Resolution ✓ ok

to have full
5 pt. curves.

TCDD Resolution ≈ 0%

HxCDD Resolution ≈ 20%

Note that the RFs used in the calculation of total homologues was ~~not~~ the average RF for the ~~one~~ isomers not the lowest RF (to overestimate amounts) as per the SOW.

STD E003076 5/1/91 16:35

Verify Continuing Calibrations.

C.C35/1,1,1 Ratio & RF ✓

$$23,7,8-\text{TCDF} \quad \text{Ratio} = \frac{A_{304}}{A_{306}} = \frac{509}{649} = 0.78 \quad \checkmark \quad \text{Reported Ratio} = 0.77 \quad (\text{page 251})$$

$$\text{RF} = \left(\frac{(509+649) \times 0.5 \text{ ng}}{(419+505) \times 0.5 \text{ ng}} \right) = 1.25 \quad \checkmark \quad \text{Reported RF} = 1.28 \quad (\text{page 251})$$

$$\text{Pe CDD} \quad \text{Ratio} = \frac{144}{92} = 1.565 \quad \checkmark \quad \text{Reported Ratio} = 1.71 \quad (\text{pg 251})$$

$$\text{RF} = \left(\frac{(144+92) \times 0.5 \text{ ng}}{(232+310) \times 0.5 \text{ ng}} \right) = 0.420 \quad \checkmark \quad \text{Reported RF} = 0.438 \quad (\text{pg 251})$$

$$\text{HxCDD} \quad \text{Ratio} = \frac{633}{491} = 1.29 \quad \checkmark \quad \text{Reported Ratio} = 1.29 \quad (\text{pg 251})$$

$$\text{RF} = \left(\frac{(633+491) \times 0.5 \text{ ng}}{(176+134) \times 0.5 \text{ ng}} \right) = 1.45 \quad \checkmark \quad \text{Reported Ratio} = 1.34 \quad (\text{pg 251})$$

<u>ISOMERS</u>	<u>Ratio of ISOMERS</u>	<u>≈ RF</u>	<u>Reported RF</u>
1,2,3,4,7,8-HxCDD	40%	1.30	1.25
1,2,3,6,7,8-HxCDD	100%	1.45	1.5
1,2,3,7,8,9-HxCDD	85%	1.23	1.28

IS

$$^{13}\text{C}_2-\text{OCDD} \quad \text{Ratio} : \frac{159}{175} = 0.91 \quad \checkmark \quad \text{Reported} = 0.90 \quad (\text{pg 252})$$

$$\text{RF} = \left(\frac{(159+175) \times 0.5}{(176+134) \times 1.0} \right) = 0.539 \quad \checkmark \quad \text{Reported} = 0.544 \quad (\text{pg 252})$$

Rec. Std.

$$^{13}\text{C}_{1,2}-1,2,3,4-\text{TCDD} - \text{Ratio} = \frac{252}{310} = 0.81 \quad \checkmark \quad \text{Reported} = 0.80 \quad (\text{pg 252})$$

<u>date(CC3)</u>	<u>Homolog</u>	<u>R.T Check</u> ✓			<u>RT shift</u>
		<u>RT Window</u>	<u>RT (CC3)</u>	<u>DAS</u>	
5/1	TCDF	18:04 → 22:50	20:55	DAS	
5/1	HxCDD	30:51 → 33:52	33:58		+4s
5/1	HxCDD	38:18 → 39:40	39:41		+1s

S/N OK ✓ 5/1/91 CC3 > 10 for all stds.

Resolution OK ✓ TCDD ≈ 5% ✓ HxCDD ≈ 20% ✓

% D OK all < 30% ✓

E003113 5/7/91 09:57 Inst. 70H

Ratios & RFs

2,3,7,8-TCDD: Ratio $\frac{698}{890} = 0.78 \checkmark$ Reported = 0.79 (page 278)

RF $\left(\frac{(698+890) \times 0.5}{(551+687) \times 0.5} \right) = 1.28 \checkmark$ Reported = 1.24 (pg. 278)

1,2,3,7,8-HxCDF: Ratio $\frac{741}{480} = 1.54 \checkmark$ Reported = 1.56 (pg. 278)

RF $\left(\frac{(741+480)}{(819+1132)} \right) = 1.60 \checkmark$ Reported = 0.69 (pg. 278)

HxCDF: Ratio $\frac{2699}{2167} = 1.24 \checkmark$ Reported = 1.23 (pg. 278)

RF $\left(\frac{(2699+2167) \times 1.25}{(827+786) \times 1.25} \right) = 2.41$ see breakdown by isomer ratio.

<u>ANALYTE</u>	by Isomer Ratios.	calc. ratio	<u>RF</u>	<u>Reported RF</u> (pg 278)
1,2,3,4,7,8-HxCDF	80%	1.93	✓	1.95
1,2,3,6,7,8-HxCDF	90	2.17	✓	2.19
2,3,4,6,7,8-HxCDF	100	2.41	✓	2.35
1,2,3,7,8,9-HxCDF	70	1.69	✓	1.62

RT

Analyte

RT

RT Window

Comments

1,2,3,4,6,7,8-HxCDF 38:51 38:52 → 41:42

(OK) other HxCDF showed identical shift of -1 sec.

S/N (OK) → 10 for all stds.

Resolution (OK) ≈ 2% TCDD ≈ 15% HxCDD

% D. (OK) ✓

CC1 stds, (5/1-E003088 5/7-E003121)

RT of Recovery stds OK

CC1 E003088 TCDD ≈ 21.24

CC3 E003076 TCDD ≈ 21.28 ✓ w/i 10 secs.

CC1 E003121 HxCDD ≈ 35.10 ✓ w/i 10 secs.

CC3 E003113 HxCDD ≈ 35.08

Ion Ratios OK

$$PeCDF = \frac{H^{540}}{H^{342}} = \frac{75}{47} = 1.596 \quad \checkmark \quad E003088$$

$$HxCDD = \frac{H^{370}}{H^{392}} = \frac{176}{135} = 1.304 \quad \checkmark \quad E003121$$

S/N OK ✓ > 2.5 for unlabelled $\approx > 10$ for labelled

III. WINDOW DEFINING MARKER

Was a window defining marker solution analyzed with the case?

	First 5/1	Isomer 5/7	Last 5/11	Isomer 5/7
TCDD	19.15	20.2	22.78	23.92
PeCDD	24.72	25.47	28.18	29.37
HxCDD	30.87	32.08	33.87	35.12
HpCDD	38.22	39.48	39.67	40.93
TCDF	18.07	19.1	22.83	23.95
PeCDF	23.07	24.22	28.43	29.58
HxCDF	29.9	31.13	34.52	35.75
HpCDF	37.60	38.87	40.47	41.7

Were the PCDD/PCDF isomers reported within the defined windows?

Actions: If any of the PCDD/PCDF congeners were outside the retention window make sure that new descriptors are used.

Window defining Mix

5/8/91 15:32 DS-5 ← Note incorrect date on sample report
 5/7/91 9:02 DS-5 Form V PCDD-1 (page 225) ~~1~~

IV. COLUMN PERFORMANCE RESOLUTION CHECK

Was the chromatographic resolution of ^{13}C -TCDDs and HxCDDs in the CC3 solution for DB-5 columns calculated for each 12 hour period?

	5/1/91	5/7/91	
% Valley ^{13}C -2378-TCDD/ ^{13}C -1234-TCDD	5%	2%	(QC limit $\leq 25\%$)
% Valley between HxCDDs	20%	15%	(QC limit $\leq 50\%$)

For SP-2331 columns:

- % Valley 1478-TCDD/2378-TCDD _____ (QC limit $\leq 25\%$)
% Valley 2378-TCDD/(1237/1238)-TCDD _____ (QC limit $\leq 25\%$)

Actions: If the peak resolution is $> 25\%$, the reviewer must use his/her professional judgement on the severity of the problem and its effect on the final results.

DFSLK)

File: E003077

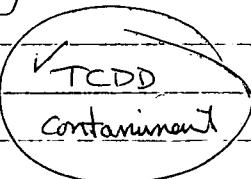
ANALYZED: 5/19/

TCDD possible contamination

$$RT = 20:56 \quad \text{window} = 19:09 \rightarrow 22:47 \quad RT = 21:41$$

- retention time does not match 2,3,7,8-TCDD \Rightarrow no apparent M-[OCl]⁺ ion.
- identification not confirmed but still possible TCDD w/in window
- must be < 5% as "noise or chemical interference" according to SDW.

$$\frac{\text{Area}_{20:56}}{\text{Area}_{21:41}} = \frac{1596.93}{4145.87} \times 100 = 38.5\% \geq 5\% \text{ limit}$$



HxCDD possible contami

$$-\text{no M-[OCl]⁺ peak} \rightarrow \text{id. not confirmed but w/in RT window}$$

$$\frac{23.87}{1376.78} \times 100 = 1.74\% < 5\% \text{ limit. } \text{No significant contamination}$$

TCDF possible contain.

- M-[OCl]⁺ ion present but RT not 2,3,7,8-TCDF but w/in TCDF window

$$\frac{47.96}{5345.91} \times 100 = .897\% < 5\%$$

Blank EMP calculation

$$\text{TCDF} \quad \frac{50\text{ng} \times 47.96 \times 1}{1\text{L} \times 5345.91 \times 1.281} = 0.350 \quad \checkmark \quad \text{Form II - PCDD pg 468 reported: 350}$$

$$\text{TCDD} \quad \frac{50\text{ng} \times 1596.93 \times 1}{1\text{L} \times 4145.87 \times 1.175} = 16.391 \quad \checkmark \quad \text{Form II - PCDD pg 468 reported: 16,391}$$

Blank EDL calculation

$$\text{PeCDF} \quad \frac{2.5 \times 50 \times (.055 + .16) \times 1}{1 \times (443 + 55.6) \times .644} = 0.042 \quad \checkmark \quad \text{Form II - PCDD pg 468 reported: 0.043}$$

$$\text{HxCDD} \quad \frac{2.5 \times 50 \times (.032 + 0.03) \times 1}{1 \times ((168 + 131) \times .90) \times 0.759} = 0.038 \quad \checkmark \quad \text{Form II - PCDD pg 468 reported: 0.038}$$

REGION I

Data Review Worksheets

VIII. FIELD DUPLICATE PRECISION

TR Nos. 6208A-01, 6208A-02

Matrix: Aquino

Matrix: Aquous
List the concentrations of the compounds which do not meet the following
RPD criteria:

1. An RPD of <30% for water duplicates.
 2. An RPD of <50% for soil duplicates.

* EMPCs

ACTIONS:

1. If the results for any compounds do not meet the RPD criteria, flag the positive results for that compound as estimated.
 2. If one value is non-detected, and one is above the CRQL:
 - a. Flag the positive result as estimated (J).
 - b. Flag the non-detected result as estimated (UJ).

NOTE: Professional judgement may be utilized to apply duplicate actions to all samples of a similar matrix.

A separate worksheet should be filled out for each field duplicate pair.

VI. MATRIX SPIKE

List percent recovery which did not meet the limits criteria.

<u>Compound</u>	<u>MS % Recovery</u>	<u>Limits</u>
TCDD	_____	60-140 50-150
PeCDD	_____	60-140
HxCDD	_____	60-140
HxCDF	_____	60-140
OCDD	_____	60-140
TCDF	_____	60-140
PeCDF	_____	60-140
HxCDF	_____	60-140
HxCDF	_____	60-140
OCDF	_____	60-140
		60-140

Actions: Recheck calculations

All % Recoveries w/in limits. Repeated results on Form III - PCDD-1 (pg. 219 of data package) are incorrect.

VII. DUPLICATE

Was a duplicate run for each matrix? An MSD.

Yes []

No []

The RPD of each analyte detected must be within 50-150% range.

Actions: Recheck all calculations if beyond the specified range. Professional judgement should be used to ascertain effect on final data.

All RPD w/i 50-150% range.

MS/MSD
RPD ✓ % Recovery all < 50% RPD.

2378-TCD

$$\frac{(44,628 \times 945) - (44,342 \times 990)}{(44,628 \times 945) + (44,342 \times 990)} = \frac{172512}{4303602} = 4.01\% \checkmark$$

Z

Form III PCDD-Z Reported = 4.01%

$$\frac{(129,184 \times 945) - (112,618 \times 990)}{(129,184 \times 945) + (112,618 \times 990)} = \frac{1058706}{11678535} = 9.07\% \checkmark$$

Z

Form III PCDD-Z Reported = 9.07%

% Recovery

$$2003114 \quad 1,23478-HxCDD (34124) \quad \frac{3425.27 \times 50}{1217.94 \times \cancel{1.005}} = \frac{121,222}{.945 L} = 128,277 \checkmark$$

$\frac{128,277}{100000 \div .945} \times 100 = 121\%$

$$123678-HxCDD (34134) \quad \frac{3717.96 \times 50}{1217.94 \times \cancel{1.005}} = \frac{116960}{.945 L} = 123,767 \checkmark$$

$\frac{123,767}{100000 \div .945} \times 100 = 117.0\% \checkmark$

$$123789-HxCDD (35109) \quad \frac{3680.83 \times 50}{1217.94 \times \cancel{1.005}} = \frac{119,45}{.945 L} = 126,406 \checkmark$$

III PCDD-3 (pg 218)
Form III PCDD-Z

(pg 221)

$$E003115 \quad 2578-TCDF (21155) \quad \frac{5352.90 \times 50}{4585.79 \times 1.281} = \frac{45,561}{.990} = 46,021 \checkmark$$

Amnt Reported correctly in (pg 221) Form III PCDD-Z
but incorrectly on Form III-PCDD-1
(pg. 219) All amounts on pg 219 are incorrect
% recovery

VIII. RECOVERY STANDARD RESPONSE

5/1

CC-3 Standard ID: E003076

Column:

Handwritten
Area Counts
Upper Limit
Lower Limit

<u>¹³C-1, 2, 3, 4-TCDD</u>	<u>¹³C-1, 2, 3, 7, 8, 9-HxCDD</u>
<u>5102 (m/e 352 = 252 m/e 334 = 310)</u>	<u>510 (m/e 402 = 176 m/e 401 = 31)</u>
<u>1124</u>	<u>620</u>
<u>281</u>	<u>155</u>

List samples which did not meet criteria.

6208A-02	¹³ C-1234-TCDD (1308)
6208A-03	" (1205)
6208A-04	¹³ C-123789-HxCDD (1317)

5/1
CC-3 Standard ID: E003113

Column:

Area Counts
Upper Limit
Lower Limit

<u>¹³C-1, 2, 3, 4-TCDD</u>	<u>¹³C-1, 2, 3, 7, 8, 9-HxCDD</u>
<u>1238</u>	<u>758</u>
<u>2976</u>	<u>1510</u>
<u>619</u>	<u>379</u>

List samples which did not meet criteria.

CC-3 Standard ID:

Column:

Area Counts
Upper Limit
Lower Limit

<u>¹³C-1, 2, 3, 4-TCDD</u>	<u>¹³C-1, 2, 3, 7, 8, 9-HxCDD</u>
<u> </u>	<u> </u>
<u> </u>	<u> </u>
<u> </u>	<u> </u>

List samples which did not meet criteria.

Example calculate is Recovery

$$\frac{3726.22 \times 50}{2272.32 \times 1} =$$

$$6208A-05 \quad \frac{(2577.15 \times 50)}{\left(\frac{(3726.22 \times 1) + 2711}{1156} \right)} = \frac{29.915}{50} = 59.8\%$$

Internal Std. Recovery Example Calculation

$$6208A-01 \ ^{10}C-OCDD \quad \frac{1852.82 \times 50}{2309.02 \times 1.566} = \frac{70.885}{100} = 70.9\% \checkmark \text{ Form I PCDD-1 (pg 18)}$$

$$6208A-02 \ ^{13}C-2378-TCDF \quad \frac{9188.60 \times 50}{5740.95 \times 1.740} = \frac{45.99}{50} = 92.0\% \checkmark \text{ Form I PCDD-1 (pg 19)}$$

$$6208A-03 \ ^{13}C-1234678-HxCDD \quad \frac{2291.51 \times 50}{2644.82 \times 1.229} = \frac{35.244}{100} = 35.2\% \checkmark \text{ Form I PCDD-1 (pg 20)}$$

$$6208A-04 \ ^{15}C-123678-HxCDD \quad \frac{864.82 \times 50}{1094.08 \times 1.989} = \frac{39.962}{50} = 79.9\% \checkmark \text{ Form I PCDD-1 (pg 21)}$$

$$6208A-05 \ ^{13}C-2378-TCDD \quad \frac{2577.15 \times 50}{3726.22 \times 1.156} = \frac{29.915}{50} = 59.8\% \checkmark \text{ Form I PCDD-1 (pg 24)}$$

$$\textcircled{+} \quad 6208A-06 \ ^{37}Cl-2378-TCDD \quad \frac{1145.12}{\cancel{1673.38} \times 50} = \frac{\cancel{1145.12}}{1.318} = \frac{44.2}{25} = 37.2\% \quad 42.0\% \checkmark$$

$$\frac{\cancel{1673.38} \times 50}{\cancel{1673.38} \times 1.318} = \frac{44.2}{25}$$

$$\textcircled{+} \quad 6208A-01 \ ^{37}Cl-2378-TCDD \quad \frac{2015.88 \times 50}{4392.05 \times 1.318} = \frac{17.112}{25} = 69.6\% \checkmark$$

- ④ Lab used incorrect RF. (1.318). This RF is listed as 1.318 in the raw data for the 5/7/91 CC3 std. but summarized in Form VII PCDD-1 as ~~1.470~~, 1.470. The CC3 for 5/1/91 is summarized as 1.583 while the raw data lists 1.369. However, the lab used 1.318 for all samples analyzed in both days.

X. TOXIC EQUIVALENT FACTOR (TEF)

Were samples with a TEF > 0.7ug/Kg for soil/sediment or fly ash; 7.0ug/Kg for chemical waste and 0.007ug/L for aqueous samples confirmed on SP-2300, SP-2331 or equivalent column?

Were EMPC values were included in the TEF calculations?

Yes [✓] No []

Check that the TEF values were calculated including EMPCs using the following guidelines: All TEF < 7 ug/L

Compound	Multiplying Factor	Concentration	Toxic Equivalent
2,3,7,8-TCDD	1.00		
Other TCDD	0.00		
2,3,7,8-PeCDD	0.50		
Other PeCDD	0.00		
2,3,7,8-HxCDDs	0.10		
Other HxCDD	0.00		
2,3,7,8-HpCDD	0.01		
Other HpCDD	0.00		
OCDD	0.001		
2,3,7,8-TCDF	0.100		
Other TCDF	0.000		
1,2,3,7,8-PeCDF	0.050		
2,3,4,7,8-PeCDF	0.500	Note that lab used 0.05 for 2,3,4,7,8-PeCDF instead of 0.5. No results affected since no EMPC > positive reported.	
Other PeCDF	0.000		
2,3,7,8-HxCDF	0.100		
Other HxCDF	0.000		
2,3,7,8-HpCDF	0.010		
Other HpCDF	0.000		
OCDF	0.001		

Total Toxic Equivalent

Reference:

"Interim Procedure for Estimating Risk Associated with Exposures to Mixtures of Chlorinated Dibenz-p-dioxins and Dibenzofurans (CDDs and CDFs)" EPA/625/3-89/016.

XI SAMPLE CALCULATION:

$$\text{Concentration (ng/g)} = \frac{\text{Qis} \times (\text{Ax}^1 + \text{Ax}^2)}{(\text{W or V}) \times (\text{Ais}^1 + \text{ais}^2) \times \text{RRFx} \times \text{D}}$$

$$\text{EDL} = \frac{2.5 \times \text{Qis} \times (\text{Hx}^1 + \text{Hx}^2) \times \text{D}}{(\text{W or V}) \times (\text{His}^1 + \text{His}^2) \times \text{RRFx}}$$

$$\text{EMPC} = \frac{\text{Qis} \times (\text{Ax}^1 + \text{Ax}^2) \times \text{D}}{\text{W or V} \times (\text{Ais}^1 + \text{Ais}^2) \times \text{RRFx}}$$

where:

Qis = quantity (ng) of appropriate internal standard added to sample before extraction

Ax¹ and Ax² = integrated areas of the two quantitation ions

W and V = weight (g) or volume (L) of sample extracted

RRFx = calculated relative response factor from the continuing calibration

Hx¹+Hx² = peak heights of the noise for the quantitation ions

His¹+His² = peak heights of the internal standard quantitation ions

D = dilution

6208A - 01

2378-TCDF

$$\text{ion ratio } \frac{5.52}{8.27} = 0.67 \checkmark$$

$$RT = 21.58' \quad CC3 = 21.55'$$

M-[EOCl] peak - unable to determine from base data.

$$\text{Conc} = \frac{(13.79)}{\frac{(5626.75 \times 50)}{(5626.75 \times 1.28)}} = 0.0956 \div 0.975 \text{ L} = 0.098 \text{ ng/L} \checkmark$$

Form I PCDD-I
(pg 18)

total TCDF

$$\text{confirmed TCDFs} \quad 19:29 \quad 303.88 \quad \text{window } 18.067 - 22.833$$

$$19:40 \quad 1159.01 \quad \text{ion ratio } 0.65 - 0.89$$

$$20:19 \quad 19.46$$

$$20:34 \quad 35.46$$

$$20:54 \quad 77.02$$

$$\frac{2378-TCDF}{\underline{1608.162}} \quad \underline{13.79} \quad \textcircled{*}$$

$$1608.162$$

$$\frac{1608.162 \times 50}{5626.75 \times 1.281} = \frac{11.159 \text{ ng}}{0.975 \text{ L}} = 11.445 \checkmark \quad \text{Form II PCDD (pg 210)}$$

EMPC
total
TCDF

~~EMPC~~

includes peaks not meeting ion ratios:

$$21:27 \quad 130.98$$

$$\underline{22:30 \quad 38.82}$$

$$169.8$$

$$\frac{1778.42 \times 50}{5626.75 \times 1.281} = \frac{12.337}{0.975} = 12.653 \checkmark \quad \text{Form II PCDD. (pg 210)}$$

12346.78-HpCDD 40:55 \checkmark CC3 40:54 ion ratio 0.91 \checkmark

$$\frac{6.99 \times 50}{1736.64 \times 1.281} = \frac{0.2457 \text{ ng}}{0.975 \text{ L}} = 0.252 \text{ ng/L} \checkmark \quad \text{Form I PCDD (pg 18)}$$

$$\frac{0.32 \times 2.5 \times 50 \text{ g}}{1.242 \times 0.975 \text{ L} \times (2826.4)} = 0.03997 \quad \text{Form I PCDD-I (pg 18)}$$

$$\begin{aligned} \text{Graphical height approx.} &= (458 + 575) \times 80\% \approx 826.4 \\ \text{Peak ratio height approx.} &= (458 + 575) \times \frac{3542.9}{4392.05} = 833.28 \end{aligned}$$

EDL
2378-TCDD

6208A -02

[TCDF]

$$\frac{21.32 \times 50}{1.281 \times 9188.6 \times 0.9902} = 0.126 \checkmark \text{ Form I PCDD-1 (pg 11)}$$

[TOTAL - TCDF]

$$\begin{aligned} \text{EMPC} &= \frac{3882.59 \times 50}{1.281 \times 9188.6 \times 0.99 L} = 16.659 \checkmark \\ \text{Conc}^{\oplus} &= \frac{3652.77 \times 50_{\text{avg}}}{1.281 \times 9188.6 \times 0.99 L} = 15.67 \checkmark \end{aligned} \quad \left. \right\} \text{Form II PCDD (pg 211)}$$

④ Ion ratios don't meet for peaks at 20:28, 21:27, & 21:40

[OCDD]

$$\text{Conc} = \frac{12.60 \times 100}{1998.25 \times 1.575 \times 0.99 L} = 0.404 \checkmark \text{ Form I PCDD-1 (pg 19)}$$

[EDL]

$$\text{PeCDD} \quad \frac{(0.12 + 0.32) \times 2.5 \times 50_{\text{avg}}}{0.632 \times (875 + 1088) \times 0.99 L} = 0.0529 \checkmark \text{ Form I PCDD-1 (pg 19)}$$

6208A -03

[OCDD]

$$\frac{33.15 \times 100}{1402.75 \times 1.575 \times 0.99} = 1.529 \checkmark \text{ Form I PCDD-1 (pg 20)}$$

[123478 HxCDD]

$$\frac{2.5 \times 50 \times (0.35 + 0.24)}{1.249 \times (196 + 151 \times \frac{989.88}{2644.82})} = 0.45 \checkmark \text{ Form I PCDD-1 (pg 20)}$$

↑ multiply by ratio of peaks
to determine height of
smaller of ≥ peaks

Total TCDD (ion ratio ~~not off~~ off)

[EMPC]

$$\frac{809.12 \times 50}{1.175 \times 2269.36 \times 0.99} = 15.325 \checkmark \text{ Form II PCDD (pg 212)}$$

Total TCDF (ion ratio ~~not off~~ off)

EMPC.

$$\frac{62.59 \times 50}{3483.46 \times 1.281 \times 0.99} = 0.708 \checkmark \text{ Form II PCDD (pg 212)}$$

[EDL]
Total PeCDD

$$\frac{(.26 + .23) \times 2.5 \times 50}{(\cancel{2269.36} \times 0.438 \times 0.99) / ((525 + 680) \times 0.4)} = \cancel{0.062} \quad 0.293 \quad \text{Not listed}$$

on Form II
PCDD (pg 212)

6208A - 04

OCDD

$$\frac{26.46 \times 100}{756.33 \times 1.575 \times 0.955} = 2.326 \quad \checkmark \quad \text{Form I PCDD-1 (pg 21)}$$

EDL

1234789 HpCDF

$$\frac{2.5 \times 100 \times (0.25 + 0.19)}{2253.91 \times 0.904 \times (159 + 149) \times 0.955} = 0.315 \quad 0.414 \quad \checkmark \quad \text{Form I PCDD-1 (pg 21)}$$

1234678 HpCDF

$$\frac{2.5 \times 100 \times (0.25 + 0.17)}{1.862 \times (159 + 149) \times 0.955} = 0.256 \quad \checkmark$$

Total TCDF

EMPC

$$\frac{114.38 \times 50}{1.281 \times 3447.94 \times 0.955} = 1.356 \quad \checkmark \quad \text{Form I PCDD-1 (pg 21)}$$

canc.

$$\frac{74.27 \times 50}{1.281 \times 3447.94 \times 0.955} = 0.880 \quad \checkmark \quad \text{Form I PCDD-1 (pg 21)}$$

Total TCDD

$$\frac{957.76 \times 50}{2272.32 \times 1.175 \times 0.955} = 18.781 \quad \checkmark \quad \text{Form I PCDD-1 (pg 21)}$$

6208A - 05

1234678 - HpCDF

$$\frac{4.19 \times 100}{3453.05 \times 1.162 \times 0.980} = 0.085 \quad \checkmark \quad \text{Form I PCDD-1 (pg 21)}$$

OCDD

$$\frac{14.98 \times 100}{1.575 \times 1492.55 \times 0.98} = 0.65 \quad \checkmark$$

HpCDF

$$\frac{945.86 \times 100}{2.431 \times 1492.55 \times 0.98} = 26.6 \quad \checkmark$$

Total TCDD

EMPC

$$\frac{1039.12 \times 50}{1.175 \times 2577.15 \times 0.98} = 17.508 \quad \checkmark \quad \text{Form II}$$

Total HpCDF

$$\frac{4.19 \times 100}{3453.05 \times 1.162 \times 0.98} = 0.085 \quad \checkmark$$

Total TCDF

$$\frac{33.05 \times 50}{3570.26 \times 1.281 \times 0.98} = 0.369 \quad \checkmark$$

6208A - 06

TOTCDD

$$\frac{871.94 \times 50}{1946.09} = \frac{19.59 \times 8100}{1.422 \times \cancel{1930.32} \times 0.95} = 0.751 \checkmark$$

TCDF EDL

$$\frac{2.5 \times 1000 \times (6.28 + 0.25)}{2.284 \times (167 + 178) \times 0.95} = 0.177 \checkmark$$

Total TCDD

$$\frac{871.94 \times 50}{1.242 \times 1946.09 \times 0.95} = 18.987 \checkmark$$

Total TCDF

$$\frac{45.05 \times 50}{1.281 \times 2679.71 \times 0.95} = 0.691 \checkmark$$